INTERFACIAL CHEMISTRY OF THE HOT WATER PROCESS FOR RECOVERING BITUMEN FROM THE ATHABASCA OIL SANDS

By

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INTRODUCTION

In the Athabasca oil sands, bitumen is separated from the quartz sand grain matrix by (at least) a thin film of water. This separation distinguishes the oil sand from other oil sands such as those found in Utah, for example. This feature is also of crucial importance to the commercial success of the hot water extraction process as it is currently being practiced in the Fort McMurray region of Alberta.

In the hot water process, oil sand is slurried with water and sodium hydroxide at about 80°C. The slurry is then conditioned in a horizontal rotating drum into which steam is injected. After conditioning the slurry is screened, then diluted with additional water and transported to a flotation vessel. In this vessel, aerated bitumen droplets float to form a froth which is subsequently collected. The greater part of the recoverable bitumen is obtained in this primary process step although froth and other streams from this vessel are further treated. Additional details can be found elsewhere (1-3).

An understanding of the mechanisms involved in the hot water process is still evolving. In view of the wide array of interfaces present in the air, oil, water, sand and clay system it is not surprising to find that interfacial phenomena appear to play a major role in the process.

It was learned at an early stage, for example, that the process is adversely affected by clay minerals, that alkaline reagents are required to maintain near neutral solutions and that the presence of surface active agents is needed (4-6). Subsequent research has demonstrated that the alkaline reagents are required principally to generate naphthenic carboxylate surfactants from the bitumen and that these surfactants are in turn the active agents in the process (7-12). It further emerges that complex interactions take place. Thus, the dosage of alkaline reagents required depends upon the fine solids (clay) content in the oil sand (10, 12).

The surfactants generated by the alkaline reagent appear not only to promote bitumen separation and aeration but to promote solids flotation as well, having thus both positive and negative contributions to the process (7-9, 11). Unifying principles of process operation which hold for the complete range of Athabasca oil sands which vary in grade, age after mining and depositional environment have thus far been elusive; Sanford's correlation between oil sand fines content and process aid requirements (12) being the closest approach which is used in practice. In this paper, we discuss some results from investigations into the role of the natural surfactants in the hot water process.

EXPERIMENTAL

Oil Sands

We will focus mainly on three oil sand samples which were used in this work. All were obtained from the Syncrude Mildred Lake oil sands operation. The compositions of these oil sands are given in Table I. In this work, the oil sands are distinguished by their bitumen content. A rich ore would contain about 12-14% (w/w) bitumen, an average grade 10-11% and a lean grade 6-9%. As the grade improves the fraction of water decreases and the relative amount of fines (clays) also decreases (12).

Bench-Scale Processing

A laboratory-scale batch extraction unit and operating procedure developed by Sanford and Seyer (10) was used for studying the oil sands hot water process. The procedure involves slurrying 500g charges of oil sand and simulates the conditioning (tumbler) step and the primary and secondary recovery steps of the continuous commercial process. Samples collected from each extraction

were assayed for oil, water and solids content by standard methods (13). From the assays, primary and secondary recoveries as well as a mass balance were obtained for each extraction. Replicate extraction samples were isolated for surfactant and electrophoretic mobility determinations.

TABLE I

COMPOSITIONS OF OIL SANDS STUDIED

Oil Sand	Bitumen	Water	Solids	Fines[a]
		(% w/w)		
Rich	13	2	85	9
Average	11	3	86	19
Lean	6	11	83	21

a. The fines level is defined as the weight fraction of
   solids smaller than 44 µm and is expressed as a
   percentage of total solids.

Primary oil recoveries obtained with this unit have been found to be good indicators of the primary oil recovery obtainable with a 2270kg/h continuous pilot unit, which is a scaled-down version of the Syncrude commercial plant.

Surfactant Determination

Secondary tailings is a process stream from the batch extractor (above) and contains the suspended clays and the bitumen not initially floated. Samples of this stream were centrifuged at 15,000 G to remove the bitumen and solids. The concentration of carboxylate-functional surfactant was then determined using a foam fractionation/acid titration technique described elsewhere (14).

The method is based on the tendency of surfactants to concentrate at interfaces. A sample is sparged with gas (such as a nitrogen/carbon dioxide mixture). The foam which is produced is then drawn off. When the process is complete all of the surfactants will have been carried over in the foam. Meanwhile, the non-surface active salts will remain present in both foam and residue. By potentiometrically titrating each phase with HCl, the total carboxylate salt content of each phase is obtained. The carboxylate surfactant concentration in the original sample can then be calculated.

Electrokinetic Determinations

Suspensions of fine solids were prepared for microelectrophoresis measurements by diluting a small portion of original secondary tailings with supernatant solution from a previously centrifuged aliquot. In some cases, a further filtration of the supernatant was required in order to remove all suspended material. In this manner, dispersions of about 0.1% or less solids were obtained in the original equilibrium solution (thus, preserving the original ionic strength and electrolyte composition).

Emulsions of bitumen in the same original equilibrium solution were prepared as follows. A sample of bitumen obtained from the Syncrude oil sands operation, having less than 1% combined solids and water, was stored at 4°C and used as a reference material. A small amount of bitumen was dispersed in the clarified secondary tailings solution with an ultrasound generator. In some cases, emulsions were prepared using instead primary froth from the corresponding batch extraction run to confirm the validity of employing emulsions prepared with the reference bitumen. The bitumen-in-water emulsions prepared had droplet radii of 4.9 ± 2.4 µm as measured using a calibrated reference grid in the microelectrophoresis apparatus microscope (using dark-field illumination).

Microelectrophoresis Measurements

The apparatus used for these studies was a Rank Brothers' Microelectrophoresis Apparatus Mark II (Rank Brothers, Cambridge, England) fitted with a rotating prism and video-viewing system. In the present work, a rectangular cell was employed, fitted with hydrogen-charged palladium electrodes. The cell was used and stored in a constantly water wet condition. Detergent washing procedures proved to be satisfactory, except for the occasional need to rinse bitumen out with toluene and then re-wet the cell.

RESULTS AND DISCUSSION

Surfactants

Of the total amount of sodium hydroxide added during processing perhaps only 5% reacts to

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produce the carboxylate surfactants (14). Figure 1 shows the relationship which is typically observed between the equilibrium concentration of carboxylate surfactants and the amount of sodium hydroxide used in the extraction. These surfactant correlations correspond to the supernatent equilibrium solution in secondary tailings slurry from the bench extractions. As indicated in the figure we commonly observe a linear relationship between the amount of sodium hydroxide added during processing and the amount of equilibrium surfactant appearing in solution. It is apparent that some oil sands yield a high concentration of surfactants in solution even when no sodium hydroxide is used while others yield low concentrations of surfactants even when fairly high levels of sodium hydroxide are employed.

Processibility curves for the oil sands investigated in the present work are given in Figure 2. They span the range of processibilities commonly observed from that for rich ore where addition of any base reduces recovery to that for lean ore where maximum oil recovery is achieved only at very high addition of base.

The relationship between the equilibrium concentration of carboxylate surfactant in solution and primary oil recovery from the bench extraction test is shown in Figure 3. In addition to the results from oil sands used in the present work, recoveries obtained in previous investigations of other grades and ages of oil sand are included for comparison. It can be seen that there exists a critical concentration of carboxylate surfactant at which maximum oil recovery is obtained from the hot water process. The value of this critical concentration is about 1.2×10^{-4} N ($\pm 15\%$). For further discussion see (14).

Interfacial Charges

In the present work, the dispersed particles and droplets can be considered to be large, with thin electrical double layers ($1 \sim 1$ to 5×10^{-3} M). By isolating process samples and reducing the solution pH it was found that the fine solids (clays) exhibited negative electrophoretic mobilities at all pH conditions (down to pH 2). In the case of the dispersed bitumen droplets, the electrophoretic mobility decreased with decreasing solution pH to an apparent isoelectric point at a pH of about 3. Similar behavior has been observed by Takamura and Chow (15). It appears that the charge at the bitumen/solution interface is primarily determined by the presence of ionized carboxylic acid groups. This would be the logical result of the generation and/or adsorption of carboxylate surfactants at this interface.

The following discussion refers to process samples isolated and studied at the equilibrium pH levels which were reached during processing.

The electrophoretic mobilities of the solids and bitumen droplets are shown as functions of the process solution pH in Figure 4. It can be seen that in general the interfacial charges increase (negative) with solution pH.

The electrophoretic mobilities of the solids and bitumen droplets are shown as functions of the process equilibrium carboxylate surfactant concentration in Figure 5. As the carboxylate surfactants will be fully ionized about pH 7, the increases in interfacial charge depicted in Figures 4 and 5 appear to be due to surfactant adsorption at the interfaces.

It appears that the solid (clay) surfaces become saturated with respect to surfactant adsorption in the range of process conditions investigated. It further appears that, in the case of the bitumen droplets, a pronounced maximum in the interfacial charge occurs as a function of surfactant concentration in the process. The surfactant concentration at which this maximum is observed is very nearly the same as the critical surfactant concentration of Figure 3.

Comparison of Figures 3 and 5 reveals that the maximum in oil recoveries and the corresponding critical surfactant concentration all correlate with a maximum in the bitumen/solution interfacial charge. We now have two common threads which apparently link oil sands and their processing behavior. That is, maximum bitumen recovery obtained using the hot water process corresponds to a single critical surfactant concentration in solution which, in turn, corresponds to a maximum in the bitumen/solution interfacial charge.

DISCUSSION

The occurrence of a maximum in the electrophoretic mobility versus surfactant concentration curve (Figure 5) indicates a marked change in the manner in which the surfactants are adsorbing at the interface. The maximum in surface charge likely corresponds to completion of a conventional monolayer coverage. It is possible that, beyond this point, some form of hemimicelle formation takes place. For the present purpose, we will consider some implications of the experimental results.

That maximum bitumen recovery from the process is associated with a maximum in the charge at the bitumen/solution interface is a rather surprising discovery and in direct contradiction to previous theories of the mechanism of the hot water process advanced by Levine (11) and by Bowman and Leja (7, 9). It is of interest to discuss how this arises.

The earlier theories cited begin with the assumption that some charging of the bitumen and solids surfaces is necessary to prevent mutual agglomeration. Beyond this requirement, they go on to predict that a minimum in bitumen surface charge will be the optimum condition for air attachment and flotation. This will be the point at which the bitumen is most hydrophobic and it was thought that hydrophobic bitumen droplets and gas bubbles attached and rose to form a bituminous froth layer. The major weakness in these treatments is the description of the carboxylic surfactant deprotonation equilibria. Here significant dissociation effects are assumed to be prominent in the solution pH range 7-10, in which the process is operated. In fact, the surfactants will be nearly fully dissociated (>90%) by a pH of 6 (see also the discussion by Hall and Tollefson (16)). The carboxylate dissociation reaction aside, Levine's prediction that a minimum in bitumen surface charge should correspond to a maximum flotation efficiency is not unreasonable if the bitumen aeration process is indeed one in which hydrophobic bitumen and air bubbles contact and adhere to each other.

The present results indicate that another mechanism is operative. Maximizing the droplet charge will reduce the hydrophobicity of bitumen. If the bitumen surface is charged by the surfactants, it is reasonable to assume that any gas (air) bubbles in the process slurry will become charged as well. The studies of Sato et al. (17) support this hypothesis.

As recognized in virtually all process mechanism theories to date, the first step in the process must be to enhance the already present-but-small separation of bitumen from the solids. Charging the bitumen/solution and solid/solution interfaces can likely generate sufficient electrostatic potentials to accomplish this. Having done so, the interfacial tension will cause the bitumen to form droplets. Conceptually, the remaining step is to selectively float the bitumen, over the solids, to form a froth. It is possible that charged air (or gas) bubbles, with an associated aqueous film, become dispersed in the bitumen. The bitumen droplets would become, in effect, globules of bituminous foam which would have a sufficiently reduced density for them to rise in the flotation vessel. The process as just described would promote bitumen flotation over solids flotation by virtue of the fact that there will be a trade-off between the repulsive forces between the air, bitumen and solid moieties and the influence of the mechanical energy which is applied in the conditioning step. The importance of optimizing mechanical energy input to the system has been emphasized by Sanford (12).

The notion that bitumen aeration consists of producing a dispersion of air or gas bubbles in the bitumen droplets is also consistent with the studies of Miller and co-authors (18-21). In Miller's studies of Asphalt Ridge bitumen in hot water processing, a zero contact angle for air-bitumen attachment was observed in the alkaline solution pH range. Having found bitumen to have lost its hydrophobicity under efficient processing conditions, these authors concluded that polar fatty acid salts (surfactants) stabilize a dispersion of air bubbles in bitumen.

CONCLUSION

The natural carboxylate surfactants generated in the hot water extraction process appear to play a critical role in determining the ultimate bitumen recovery. There apparently exists a single equilibrium solution concentration of surfactant which corresponds to maximum oil recovery from the process. This relationship appears to hold irrespective of factors such as the oil sand's grade, age after mining or depositional environment.

It has also been shown that natural surfactants adsorb at the mineral and bitumen surfaces. The interfacial charges increase, in general, with increasing solution pH and surfactant concentration. The bitumen/solution interfacial charge, however, passes through a distinct maximum and is entirely determined by surfactant adsorption.

The maximum in bitumen droplet charge corresponds to the critical surfactant concentration for maximum bitumen recovery from the process. This means that maximum recovery in the process is not associated with minimum surface charges as had previously been supposed.

The present results support a theory of the hot water process in which electrostatic forces drive the separation of bitumen from the oil sand matrix and in which bitumen is aerated by a dispersive rather than an attachment mechanism.
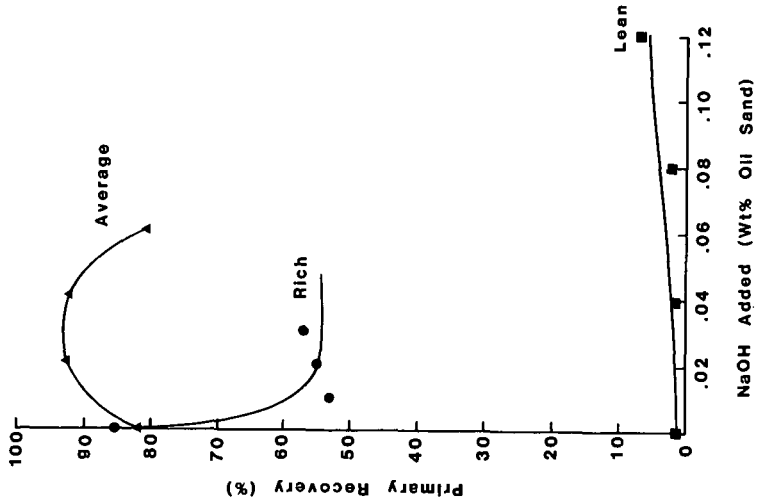
ACKNOWLEDGMENTS

Figure 1. The equilibrium concentrations of carboxylate surfactant produced in processing oil sands by using various amounts of sodium hydroxide. The data refer to process stream extracts.
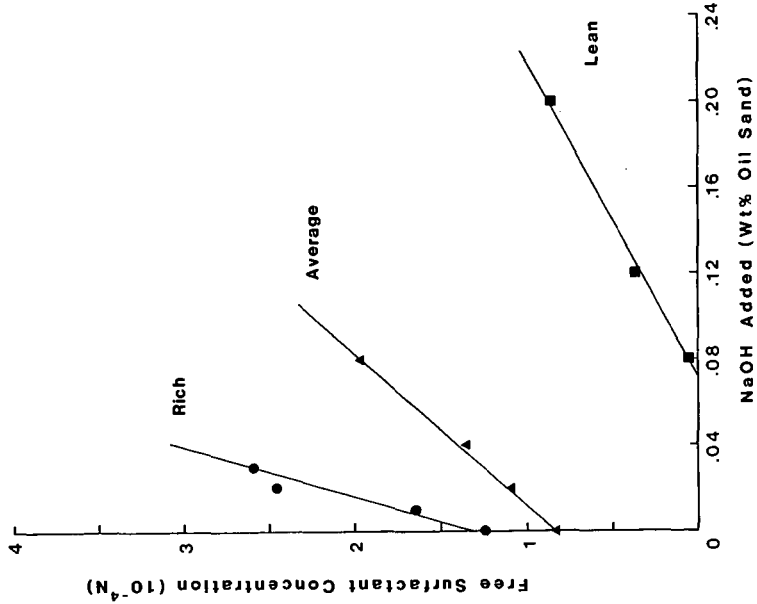
Figure 2. Processibility curves for three oil sands as obtained from laboratory scale batch extractions.
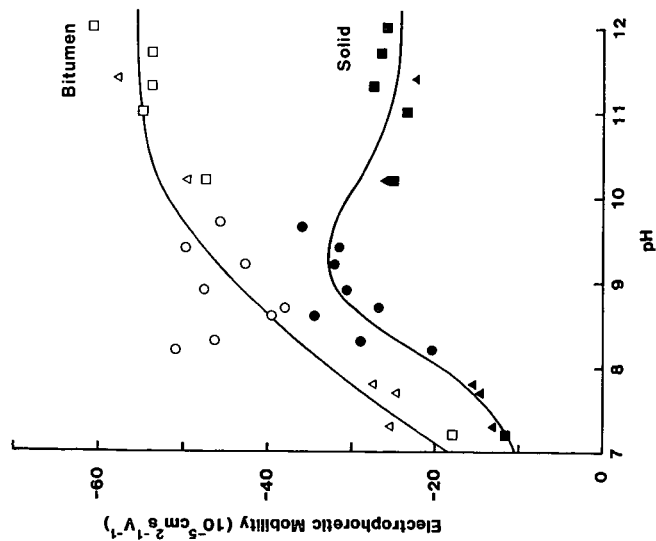

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Figure 3. Primary oil recoveries obtained from processing various oil sands versus the equilibrium carboxylate surfactant concentrations observed in process stream extracts. The symbols indicate the rich (●), average (▲) and lean (■) ores of the present work.

Figure 4. Electrophoretic mobilities observed for fine solids (filled symbols) and bitumen droplets (open symbols) as functions of process solution pH. The data are for average (●,○), lean (▲,△) and a mixture of the average and lean (■,□) ores extracted at various NaOH addition levels.

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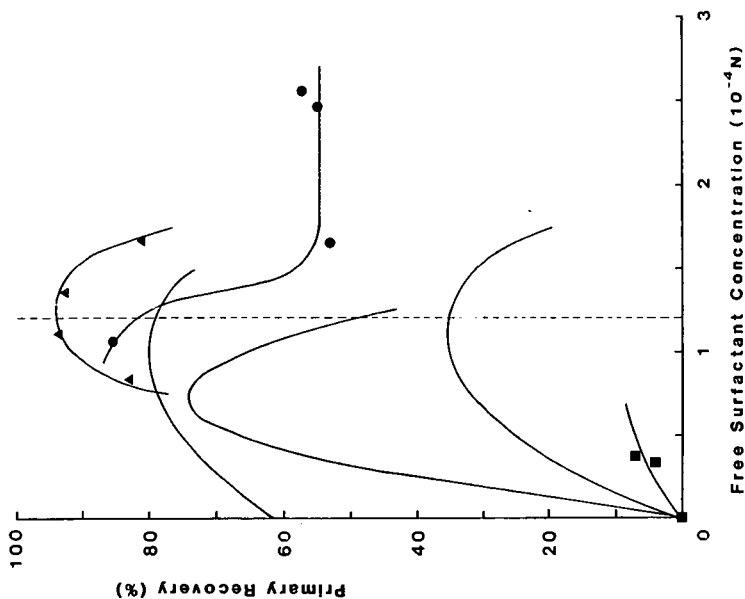
Figure 5. Electrophoretic mobilities of fine solids (filled symbols) and bitumen droplets (open symbols) as functions of the equilibrium carboxylate surfactant concentration in process stream extracts. The data are for average ($\bullet$,$\circ$) lean ($\blacktriangle$,$\triangle$) and a mixture of the average and lean ($\blacksquare$,$\square$) ores extracted at various NaOH addition levels.
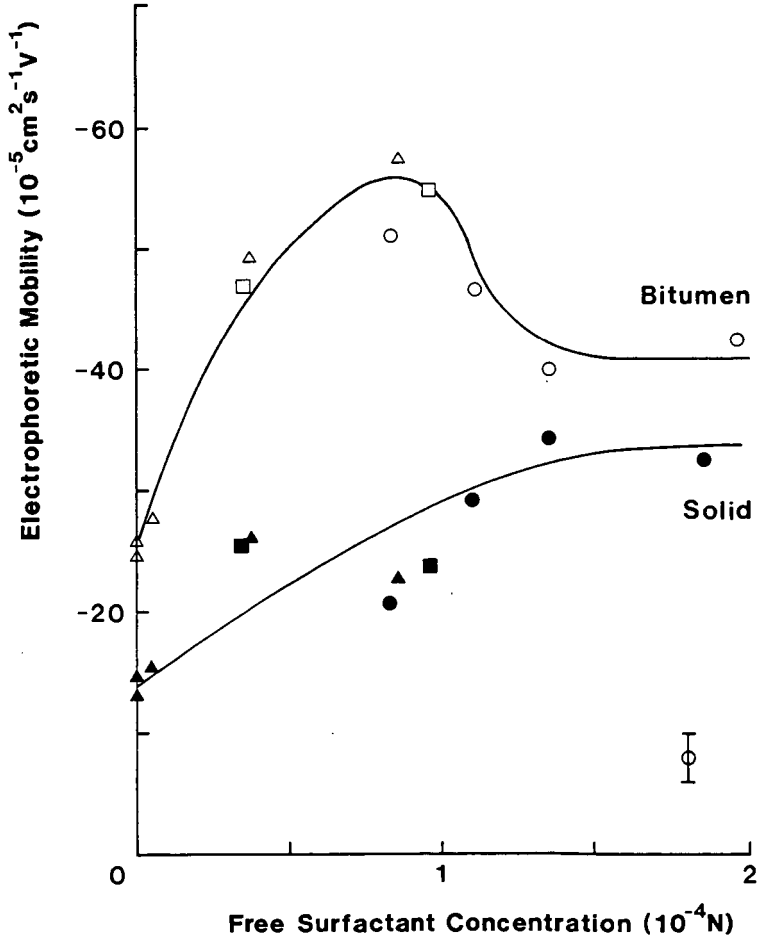
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